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ULTRASONIC VELOCITY IN BINARY MIXTURES UNDER HIGH PRESSURES AND THEIR THERMODYNAMIC PROPERTIES I

—Binary Mixture for Nitrobenzene-Aniline—

BY TOSHIHARU TAKAGI

The ultrasonic velocities in a binary mixture of liquid nitrobenzene and aniline were measured at temperature 30°C and pressures up to freezing pressures or 2100 bar (10^5Pa) by a pulse technique of fixed-path type at a frequency of 1 MHz, with an estimated error of less than 0.3 percent.

The ultrasonic velocities in a binary mixture at atmospheric pressure increase with increasing mole fraction of aniline, but the data at near 0.5 mole fraction of aniline deviated from the smooth curve. The ultrasonic velocity is found to increase parabolically with increasing pressure.

Using the measured values of ultrasonic velocity and the P-V-T relations reported in the literature, the adiabatic compressibility, the specific heat ratio and the specific heat at constant pressure have been derived under each condition. At atmospheric pressure, the results for pure liquids were in a good agreement with experimental values in the literature. It was also found that the measured values of ultrasonic velocity showed an unusual behavior indicating the existence of some intermolecular interactions between nitrobenzene and aniline.

Introduction

The ultrasonic velocity in fluid is one of the important physico-chemical properties, and it has been systematically studied in pure liquids or binary mixtures at atmospheric pressure[1,2]. There are also a number of papers on the measurements of ultrasonic velocities and some thermodynamic properties for pure liquids under high pressures[3~6]. These values under high pressure, which can be determined experimentally with high accuracy, give a powerful clue to the investigation of the thermodynamic properties of liquids. However, the detailed measurements for binary liquid mixtures are rarely reported, except a binary mixtures of water and alcohol.

Therefore, the author is studying some thermodynamic properties of binary mixtures measuring ultrasonic velocities under high pressures. In this paper, the ultrasonic velocity in nitrobenzene-

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aniline mixtures, the P-V-T relations of which were given by Gibson *et al.*[7], were measured at temperature of 30°C and pressures up to the freezing pressures or 2100 bar. Using the experimental values of the velocity and the P-V-T relations, the adiabatic compressibility, the specific heat ratio and the specific heat at constant pressure were calculated, and their compositions or pressure dependencies examined.

Experimental

The method used for measurements of ultrasonic velocity was a pulse technique of fixed-path type[8] at a frequency of 1 MHz, and two x-cut quartz crystals were fixed parallel each other in a high pressure vessel. The ultrasonic velocity was obtained by measuring the time required to travel the distance between two transducers, and the travelling time was measured by an electric time interval counter. At each experimental condition, the pressure was read by two Bourdon gauges (Heise Bourdon Tubes) of the pressure range up to 10000 psi and 50000 psi, which were calibrated by a dead weight tester. The high pressure vessel was immersed in a liquid thermostat bath controlled within ±0.01°C. The uncertainty in the measurements of ultrasonic velocity was estimated to be less than 0.3 percent over the whole range of the experiment.

Materials: Pure nitrobenzene and aniline were obtained from Wako Pure Chemical Ltd. (G. R. Grade) and their densities were 1.1935 and 1.0132g · cm^{-3}, and refractive indices were 1.5478 and 1.5769 at 30°C, respectively. The compositions of the binary mixture are chosen to six compositions, namely 0.1668, 0.3050, 0.4311, 0.6842, 0.7984 and 0.8909 mole fraction of aniline, for which the P-V-T relations were reported by Gibson *et al.*[7] The composition was determined by the weighing method, within the accuracy of 0.03 percent.

Results and Discussions

Ultrasonic velocity

The experimental values of the ultrasonic velocity in the binary mixtures of nitrobenzene-aniline at 30°C at atmospheric pressure are plotted in Fig. 1. The velocity increases with increasing mole fraction of aniline, but the curvature at near half concentrations deviates a little from the smoothed curve. The velocities in pure nitrobenzene and aniline are found to agree well with the values given by Coppens *et al.*[9] and Desphande *et al.*[1], within the accuracy of 0.2 percent. The deviated values from the smoothed curve at near half concentrations are 9.23m · sec^{-1} (0.6%), and therefore the author believes that the abnormal feature at these compositions is significant. The

7) R. E. Gibson and O. H. Loeffer, *J. Amer. Chem. Soc.*, **61**, 2877 (1939)
8) T. Makita and T. Takagi, *This Journal*, **38**, 41 (1968)
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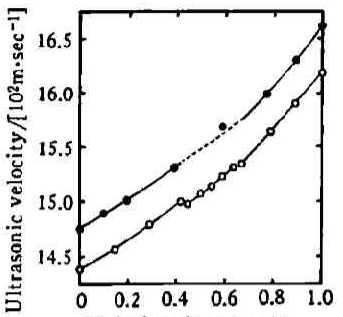

Fig. 1 Composition dependency of the ultrasonic velocity in nitrobenzene-aniline mixtures at atmospheric pressure
○: 30°C This work
●: 25°C Gabrielli[10]

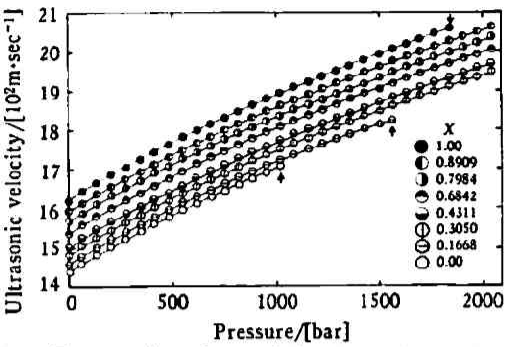

Fig. 2 Pressure dependency of the ultrasonic velocity in nitrobenzene-aniline mixtures at 30°C
†: Freezing pressure

Table 1 The coefficients of ultrasonic velocity and the maximum deviation at 30°C, and the freezing pressure

$c/[\mathrm{m \cdot sec^{-1}}] = A_1 + A_2P + A_3P^2$ [P in bar]

Mole fraction of aniline	A_1	$10A_2$	-10^5A_3	Max. dev. [%]	Freezing pressure/[bar] 10°C	30°C
0.00	1437.0	3.1208	5.258	0.07	192± 6	1074± 5
0.1668	1455.6	3.0649	4.763	0.09	677± 5	1637±14
0.3051	1480.0	3.0142	4.309	0.25	1241±12	—
0.4312	1501.6	2.9599	3.731	0.27	2286± 4	—
0.6842	1535.4	2.9442	3.268	0.28	—	—
0.7984	1566.1	2.8863	3.173	0.24	1551±28	—
0.8909	1591.8	2.9014	3.141	0.18	1168±12	—
1.00	1623.0	2.9867	3.595	0.12	897± 8	1885± 6

literature values[10] at 25°C are also shown in the figure and the results exhibit the similar tendency with present data at 30°C.

Figure 2 shows the relationships between the ultrasonic velocity and the pressure for nitrobenzene-aniline at 30°C, and X is the mole fraction of aniline in the mixtures. The velocity at each composition increases parabolically with increasing pressure over the whole range of the present experiment. Consequently, the experimental results are used to determine the coefficients in the quadratic equation, by means of the least square method. The values of the coefficient and the maximum deviation are listed in Table 1.

The freezing pressure has been determined at the point where the ultrasonic wave is attenuated and so the measurements become impossible. The results are also listed in this Table. As can be seen from those values (at 30°C), the freezing pressure of this mixture is remarkably higher than

10) I. Gabrielli and G. Polani, *Ricerica Scientifica*, **24**, 1039 (1954)

that of pure nitrobenzene in spite of small addition of aniline (X=0.1668). However, at 30°C, it was impossible to determine the freezing pressures over the whole compositions. Therefore, the freezing pressures of mixtures were also determined at 10°C, and the results are listed together in Table 1. One can see that the freezing pressure was remarkably increased as the composition approaches to equimolar one, and at the composition of 0.6842, the freezing was not observed even at 3000 bar.

As a measure for the pressure dependency of the ultrasonic velocity, there is Rao's rule which combines the ratio of $(\partial c/\partial P)_T/c$ with the isothermal compressibility, κ_T by equation (1):

$$\frac{(\partial c/\partial P)_T}{c\kappa_T} \simeq 4, \qquad (1)$$

where c is the ultrasonic velocity, P is the pressure. This relation has been well confirmed for pure organic liquids[11].

For nitrobenzene-aniline mixtures, the relationships between $(\partial c/\partial P)_T/c$ or κ_T and the composition of X are plotted in Fig. 3, in which κ_T was calculated using the P-V-T data[7]. The values of $(\partial c/\partial P)_T$ in Fig. 3 have been obtained from the values of velocity at pressure up to about 300 bar. Using the data in this figure, the values of $(\partial c/\partial P)_T/c\kappa_T$ were calculated and the results were about 3.9~4.5. The composition dependencies of κ_T and $(\partial c/\partial P)_T/c$ also indicate the some unusual behavior at near equimolar composition. Further, integration of equation (1) gives:

$$c = A\rho^4, \qquad (2)$$

were A is the constant, and the relations of equation (2) are shown in Fig. 4 using the measured velocity c and the density ρ in the literature at pressures up to 1000 bar. As can be seen in this figure, the results for each composition are approximately satisfied with the linear relations, and the

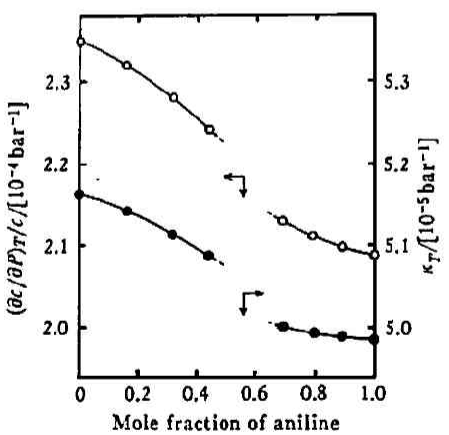

Fig. 3 Composition dependency of $(\partial c/\partial P)_T/c$ and the isothermal compressibility for nitrobenzene-aniline mixtures at 30°C and atmospheric pressure
○: $(\partial c/\partial P)_T/c$
●: κ_T

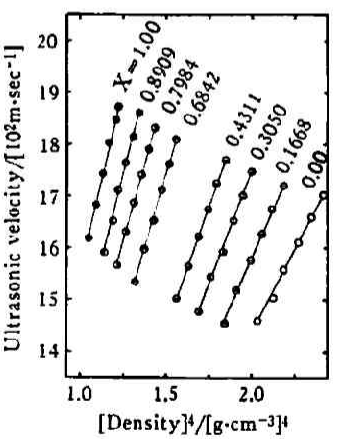

Fig. 4 Density dependency of the ultrasonic velocity under high pressure in nitrobenzene-aniline mixtures at 30°C

11) H. Nomura, A. Kuroki and Y. Miyahara, *J. Acoust. Soc. Japan*, **27**, 524 (1971)

velocities are expected to be about zero when the density would be reduced to zero. Consequently, one can conclude that the data of the ultrasonic velocity have been measured with a good accuracy.

On the other hand, for pure liquids, the author reported[5] that the velocity increases linearly with increasing density at pressure ranges from 1 to 2100 bar, and the following equation can be deduced:

$$c=B\rho+C \qquad (3)$$

were B and C are constants. As shown in Fig. 5, the relationships between the velocity and the density also shows the linear function in nitrobenzene-aniline mixtures at 30°C. And, it is found that the linear relations of equation (3) were more favorable than that of equation (2) for representing the results under the present experimental condition.

Adiabatic compressibility

From the values of the ultrasonic velocity, c and the density, ρ, the adiabatic compressibility, κ_S has been calculated by equation (4):

$$\kappa_S=1/(\rho c^2). \qquad (4)$$

The results for nitrobenzene, aniline and their mixtures are shown in Fig. 6. Gibson *et al.* measured the P–V–T relation of their mixtures at temperatures of 25 to 85°C and pressures up to 1000 bar, and reported the parameters of the Tait equation. If the relation of equation (3) holds for the higher pressure region, one can calculate the densities above 1000 bar using the values of the experimental ultrasonic velocity. The accuracy of the values of κ_S would be better than the order of 2 percent.

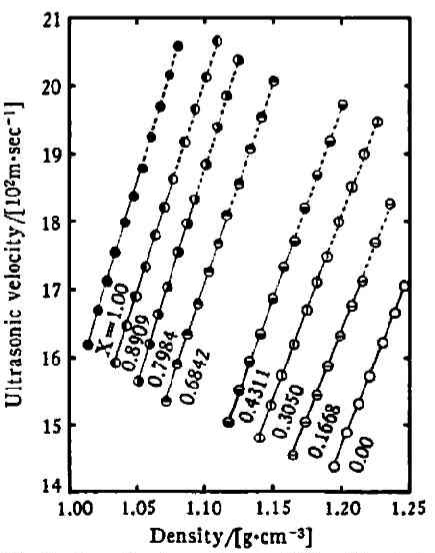

Fig. 5 Density dependency of the ultrasonic velocity under high pressure in nitrobenzene-aniline mixtures at 30°C

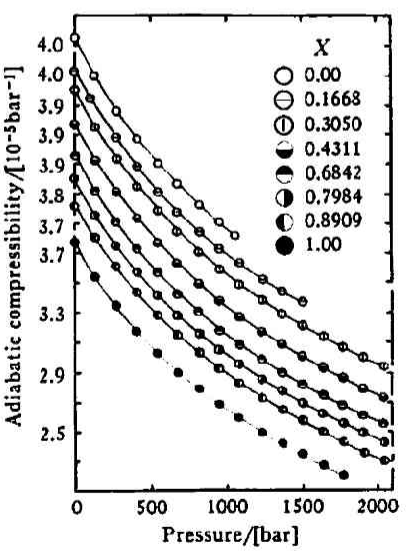

Fig. 6 Pressure dependency of the adiabatic compressibility for nitrobenzene-aniline mixtures at 30°C

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Specific heat ratio

The specific heat ratio, γ can be expressible by the following equation :

$$\gamma = C_P/C_V = \kappa_T/\kappa_S = \rho c^2 \kappa_T. \qquad (5)$$

And the values of γ is plotted against pressure as shown in Fig. 7. The values of γ decrease linearly with increasing pressure. However, the relation between γ and the mole fraction of aniline shows an abnormal behavior, namely γ increases with the increase of aniline composition at first, and then drops at the nearly equimolar composition following monotonous increases with increasing composition.

Specific heat at constant pressure

From some thermodynamic properties, the specific heat at constant pressure, C_P can be derived by the following equation :

$$C_P = \frac{T\alpha^2 c^2}{\gamma - 1}, \qquad (6)$$

where α is the expansion coefficient, and was calculated using the P-V-T relations[7]. The pressure dependency of C_P thus obtained are plotted in Fig. 8. The calculated values for pure liquids at atmospheric pressure are found to agree with the literature values[12,13] satisfactorily. As can be seen, the C_P value decreases with increasing pressure in the lower pressure range, and after passing through the minimum point at approximately 600 bar, it increases with increasing pressure. In the case of binary solutions the C_P values were also calculated and they showed monotonous increase as the concentration of aniline increased, except at the region between X=0.4311 and 0.6842 where a little deviation from the smoothed curve was observed. The same tendency was also observed in this system[14].

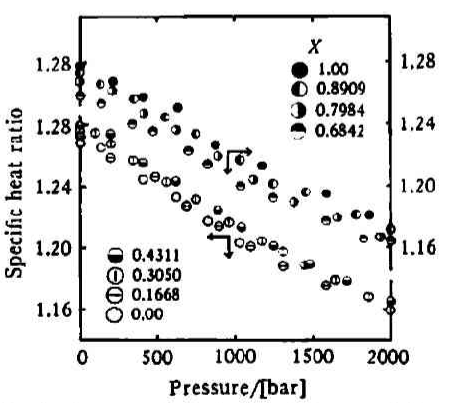

Fig. 7 Pressure dependency of the specific heat ratio for nitrobenzene-aniline mixtures at 30°C

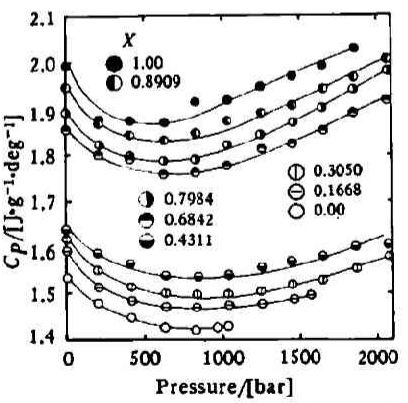

Fig. 8 Pressure dependency of the specific heat at constant pressure for nitrobenzene-aniline mixtures at 30°C

12) G. S. Parks and S. S. Todd, *J. Chem. Phys.*, **2**, 440 (1934)
13) W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull, *J. Chem. Eng. Data*, **7**, 229 (1962)
14) "*International Critical Tables*", V, p. 128, McGrow-Hill, New York (1928)

In general, the values of the partial molar quantities have been used to discuss the properties of the mixed system. Therefore, the partial molar specific heat at constant pressure, $\bar{C}_P$ for the binary mixture of nitrobenzene-aniline was calculated at atmospheric pressure. And the obtained result showed that the composition dependency of $\bar{C}_P$ was nearly the same as that of an ideal solution at the nitrobenzene-rich region, while it was like a nonideal solution at the aniline-rich region. However, the number of data was very few and it can be said that the present conclusion has only a qualitative meaning.

When nitrobenzene and aniline are mixed, their color change to the deep orange show that some intermolecular interaction occurs. This might be one of the origin of the peculiar behavior of the system of nitrobenzene-aniline. From the facts presented above, it is concluded that the system of nitrobenzene-aniline shows the behavior of a nonideal solution.

However, it is insufficient to explain quantitatively the concentration dependency of the specific heat at constant pressure especially at 0.4311 and 0.6842 mole fraction of aniline. Consequantly, the detailed measurements are expected in future, particularly in the nearly equimolar solution.

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